Journal of Innovative Materials in Extreme Conditions
2021
Volume 2
Issue 2

AB INITIO INVESTIGATIONS AND BEHAVIOUR OF THE α-Ce_2ON_2 PHASE IN THE EXTREME PRESSURE CONDITIONS

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Abstract: *Recently predicted α-phase in the Ce_2ON_2 compound has been further investigated using ab initio methods. The structural properties of the α-Ce_2ON_2 have been investigated and compared with the related* $AlCo_2Pr_2$ structure. *Mechanical properties including elastic constants, bulk, shear and elastic moduli, Poisson's ratio, Pugh's criterion, and hardness are calculated in the pressure range from 0 to 10 GPa. Also, electronic properties are calculated at the same pressure conditions using DFT-LDA approximation and the characteristic band structure has been analyzed.*

Keywords**:** *α-Ce_2ON_2, ab initio, mechanical properties, electronic properties, high pressure*

1. Introduction

When investigating the materials under extreme conditions it is important to know the energy landscape concepts for chemical systems under extreme conditions, as well as materials properties investigation under extreme conditions.[1-3] Nitrogen doping is often used for oxide photocatalysts if band-gap tuning is needed.[4] In this way obtained stoichiometric oxynitrides can have useful optical properties.[5] Furthermore, the incorporation of nitrogen has been reported as an alternative method for cation doping that increases the anion vacancy concentration and stabilizes the cubic or tetragonal form of ZrO_2 at room temperature.[6] The nitrogen-doped oxides exhibit good mechanical, catalytical, and optical properties and have been reported as superionic conductors.[6]

On another side, pure ceria (CeO_2) has important technological applications, e.g., as catalysts, in electrolyte solid oxide fuel cells, oxygen storage components, mechanical polishing for microelectronics, metallurgy, and biomedicine.[7-11]. Doping of ceria with nonmetals is extremely rare, but it has been reported before, where that doping significantly changes the physical and chemical properties of ceria [12-14]. Besides doping with nitrogen, ceria has been doped with carbon, phosphorus, sulfur, magnesium, lanthanum, europium, and praseodymium.[15-18] Similarly, cerium nitride (CeN) is a material with interesting optical, electronic, and magnetic properties, related to the structure and oxidation state.[19-21]

In our previous study, we have identified stable and metastable modifications of the Ce_2ON_2 compound for the first time, using a combination of global optimization and data mining. [22] The α-Ce_2ON_2 modification, with the post-$AlCo_2Pr_2$ structure, is predicted to be the thermodynamically stable modification at standard conditions. In this work, we go one step forward giving the predicted structural, mechanical, and electronic properties in the high-pressure range for the not-yet-synthesized α-Ce_2ON_2 phase.

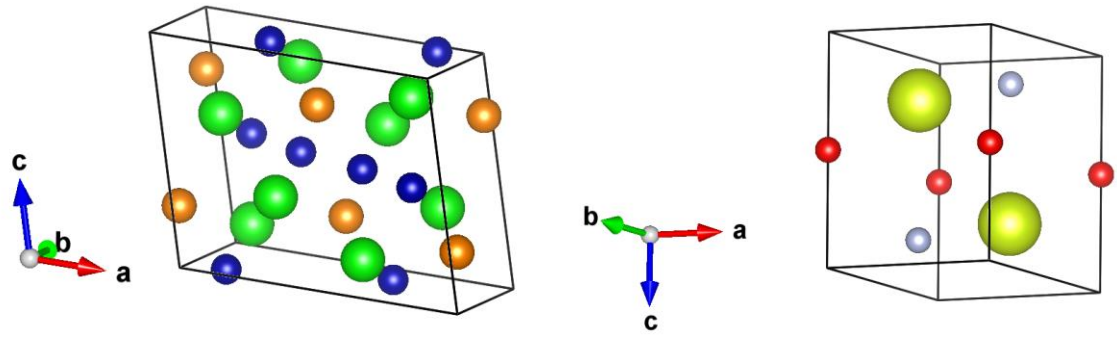
2. Computational details

Ab initio calculations of the mechanical and electronic properties in the high-pressure regime were performed using the CRYSTAL17 code [23], which is based on linear combinations of atomic orbitals. Local optimizations are performed on the density functional theory level using the local

density approximation (LDA). In the case of Ce^{4+} a pseudopotential [24] was used, together with a [*4s4p2d3f*] basis set, for O^{2-} a [*4s3p*] basis set was used [25, 26], and for N^{3-} [*3s2p*] an all-electron basis set based on Gaussian-type orbitals was employed [27, 28]. A computational strategy implemented in the CRYSTAL solid-state quantum-chemical program has been performed for the accurate *ab initio* simulation of elastic properties of crystalline materials under pressure.[29] Full elastic tensor has been generated by using the keyword ELASTCON. [30, 31] Crystallographic analysis was performed using KPLOT code,[32] and structure visualization using VESTA software [33].

3. Results and Discussion

Figure 1a shows the parent structure obtained from data mining based searches in the ICSD database [34] in the $AlCo_2Pr_2$ type of structure [35]. It crystallizes in the monoclinic space group *C2/c* (no. 15) with 8-fold coordination of cobalt by Al and Pr atoms (Table 1). The structure evolved after *ab initio* structure optimization into α-Ce_2ON_2 phase, with so-called post-$AlCo_2Pr_2$ type of structure, shown in Figure 1b. The new α-phase shows trigonal symmetry with the *P-3m1* space group (no. 164) and details considering unit cell parameters and atomic positions are published elsewhere. [22]



a) b)

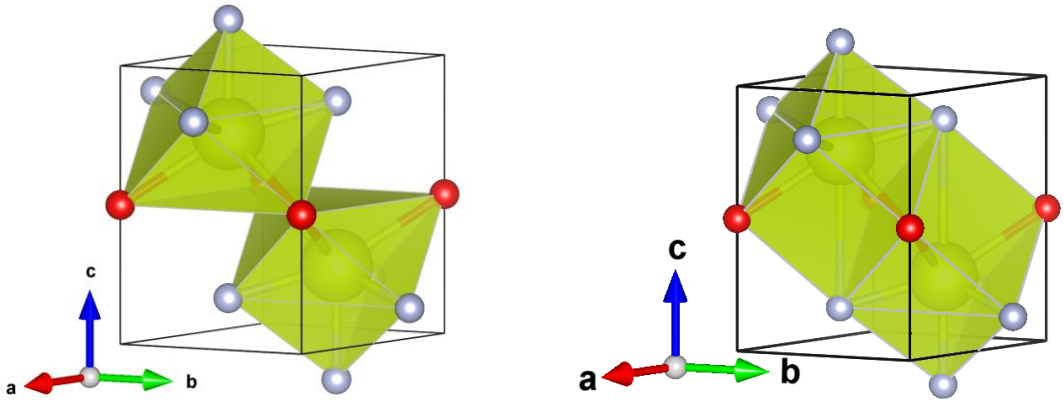
Figure 1. Crystal structure of a) $AlCo_2Pr_2$ type, where aluminum atoms are orange color, cobalt atoms are blue, and praseodymium atoms are green, b) α-Ce_2ON_2 phase, where cerium is yellow, oxygen is red, and nitrogen is shown as grey balls.

Table 1. Atom distances and coordination of cobalt in the $AlCo_2Pr_2$ structure, and cerium in the α-Ce_2ON_2 structure.

Co-coordination/Atom	$AlCo_2Pr_2$ (Å)	Ce-coordination/atom	α-Ce_2ON_2 (Å)
Al	2.5714	N	2.2536
Al	2.5879	N	2.2536
Pr	2.9613	N	2.2536
Pr	2.9778	N	2.2752
Pr	2.9778	O	2.5674
Pr	3.0270	O	2.5674
Pr	3.0521	O	2.5674
Pr	3.0618	N	3.2944

Interestingly is that the cerium atoms are in 7-fold coordination with four nitrogen and three oxygen atoms in the α-Ce_2ON_2 phase with the polyhedra edge-connected (Figure 2a). However, when including the second coordination polyhedra of cerium atom (distances up to 4 Å), one can observe

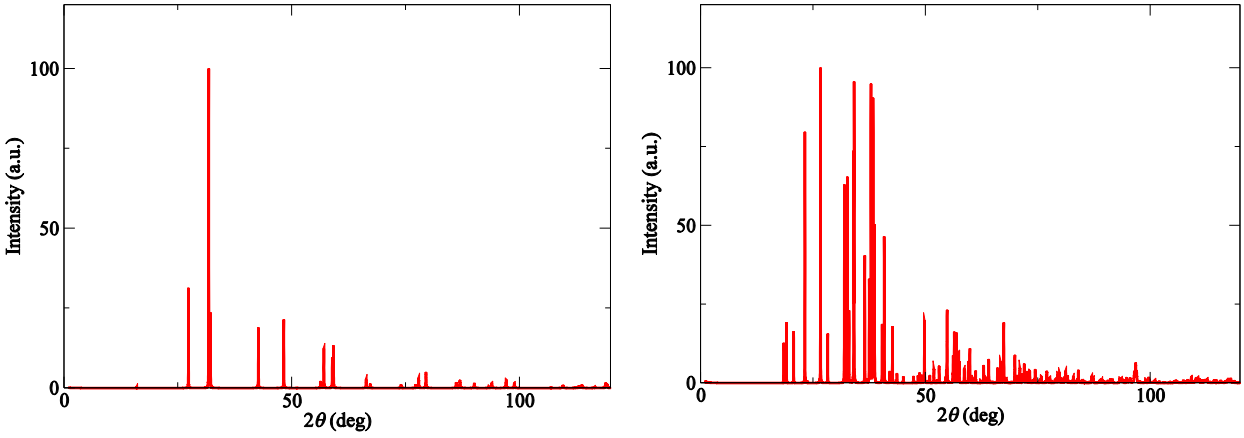
distant nitrogen atom at 3.2944 Å (Table 1). When plotting an additional N atom, the Ce atom becomes 8-fold coordinated in the α-phase with a square prism connected by planes (Figure 2b).



a) b)

Figure 2. Crystal structure of α-Ce_2ON_2 phase with a) 7-fold coordination; b) 8-fold coordination of cerium atoms by O- and N-atoms. Note that cerium is yellow, oxygen is red, and nitrogen is shown as grey balls.

Since the α-Ce_2ON_2 structure is only theoretically predicted phase in the Ce_2ON_2 system, future experimental work is expected. In this respect, we show theoretical X-ray diffraction patterns (XRDP) of α-Ce_2ON_2. which could be used for the identification of α-Ce_2ON_2 (Figure 3a). Moreover, in Figure 3b, we show the experimental XRPD of the parent $AlCo_2Pr_2$ type, clearly different from the predicted α-phase of the Ce-O-N compound.



a) b)

Figure 3. X-ray diffraction patterns (XRDP) of: a) theoretically predicted α-Ce_2ON_2 phase; b) experimentally observed $AlCo_2Pr_2$ type of structure.

In our investigation, we have calculated elastic constants C_{ij} for the investigated α-Ce_2ON_2 compound up to 10 GPa, in order to get insight into the mechanical stability. Second-order elastic constants for α-Ce_2ON_2 candidates are given in Table 2. It is known from the literature that

eigenvalues of the elastic constant matrix should be all positive in order to have mechanically stable structure. [36] Since this condition is satisfied, the α-Ce_2ON_2 phase should be the mechanically stable phase.

Relation between bulk and shear modulus was calculated to connect the mechanical and elastic properties of the α-Ce_2ON_2 modifications. This simple relation B/K is called Pugh's criterion [37]. According to this criterion, its critical value of 1.75, separates ductile from brittle materials. In the cases when this value is above 1.75, the material exhibits ductile behavior. In contrast, the materials with values of Pugh's criterion under 1.75 have a brittle character. Thus, calculated Pugh's criteria are given in Table 3 and according to them, α-Ce_2ON_2 exhibits ductile behavior. Another insight into ductile/brittle behavior comes from Poisson's ration v. For the values of v smaller than 0.26, the material is expected to have brittle behavior. In this context, we note that according to this criteria α-Ce_2ON_2 has ductile nature. To conclude regardless of the applied criterion (Pugh's or Poisson's), the α-Ce_2ON_2 phase exhibits ductile character, which is important for its future technological applications. This trend continues for the whole investigated pressure range.

Furthermore, hardness V_H is related to the elastic and plastic properties of materials, and can be calculated starting from bulk modulus B and shear modulus K according to equation (1) from Ref. [38]:

$$V_H = 0.92(K/B)^{1.137}K^{0.708} \quad (1)$$

Table 2. The calculated elastic constants of α-Ce_2ON_2 modifications up to 10 GPa.

Pressure (GPa)	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}
0	312.21	180.08	120.02	169.97	103.97
1	318.60	184.60	124.32	174.50	106.08
2	325.18	188.90	129.94	181.98	109.54
3	330.73	192.80	134.63	188.35	111.99
4	337.29	197.02	139.66	189.44	114.70
5	343.31	200.53	143.75	194.50	117.06
6	349.37	204.30	148.63	203.23	119.66
7	355.64	208.20	152.61	209.97	121.99
8	361.73	211.69	156.21	217.16	123.91
9	367.66	215.19	159.88	222.15	125.62
10	373.10	219.05	163.97	230.05	127.55

Table 3. Bulk modulus B (GPa), shear modulus K (GPa), Young's modulus E (GPa), Poisson's ratio (v), hardness V_H (GPa), and Pugh's criterion,B/K, calculated with LDA in the α-Ce_2ON_2 up to 10 GPa.

Pressure (GPa)	B	K	E	v	V_H	B/K
0	168.18	72.62	190.46	0.31	7.36	2.32
1	172.85	74.14	194.60	0.31	7.41	2.33
2	178.94	76.28	200.38	0.31	7.51	2.35
3	184.10	77.89	204.80	0.32	7.55	2.36
4	187.85	79.20	208.32	0.32	7.61	2.37
5	192.38	80.91	212.88	0.32	7.71	2.38
6	198.41	82.87	218.23	0.32	7.79	2.39
7	203.49	84.71	223.16	0.32	7.87	2.40
8	208.47	86.52	228.02	0.32	7.96	2.41
9	212.66	88.01	232.02	0.32	8.03	2.42
10	218.02	89.51	236.20	0.32	8.06	2.44

Calculated hardness V_H for the investigated α-Ce_2ON_2 modification in the pressure range 0-10 GPa is given in Table 3. The hardness increases with the applied pressure. In principle, Bulk modulus *B*, shear modulus *K*, Young's modulus *E*, increase more rapidly with the increase of pressure, while Poisson's ratio (***ν***), hardness (V_H), and Pugh's criterion (*B/K*), increase more gradually within the same pressure range (Table 3). The mechanical properties of α-Ce_2ON_2 under pressure are very interesting for their scientific and future industrial application.

Electronic properties of the α-Ce_2ON_2 are investigated theoretically. The compound is a semiconductor, with an indirect band gap of ~1.11 eV, with a tendency of the band gap transition from indirect to direct band gap along the H-K special points of the Brillouin zone. Band structure calculation of the α-Ce_2ON_2 has been performed using DFT-LDA functional (Figure 4).

In order to investigate the effect of pressure on the electronic properties of the α-Ce_2ON_2, its behavior up to 10 GPa was investigated. The band gap value at 0 GPa is 1.11 eV and increases linearly with pressure up to 1.17 eV at 10 GPa. Although the band gap widens with the pressure it remains indirect for the whole pressure range. This can be very important for possible band gap tuning of α-Ce_2ON_2 at high pressures, especially since possible change of a direct and indirect band gap indicates applications in e.g. photovoltaics (solar cells) and light-emitting diodes (LEDs).

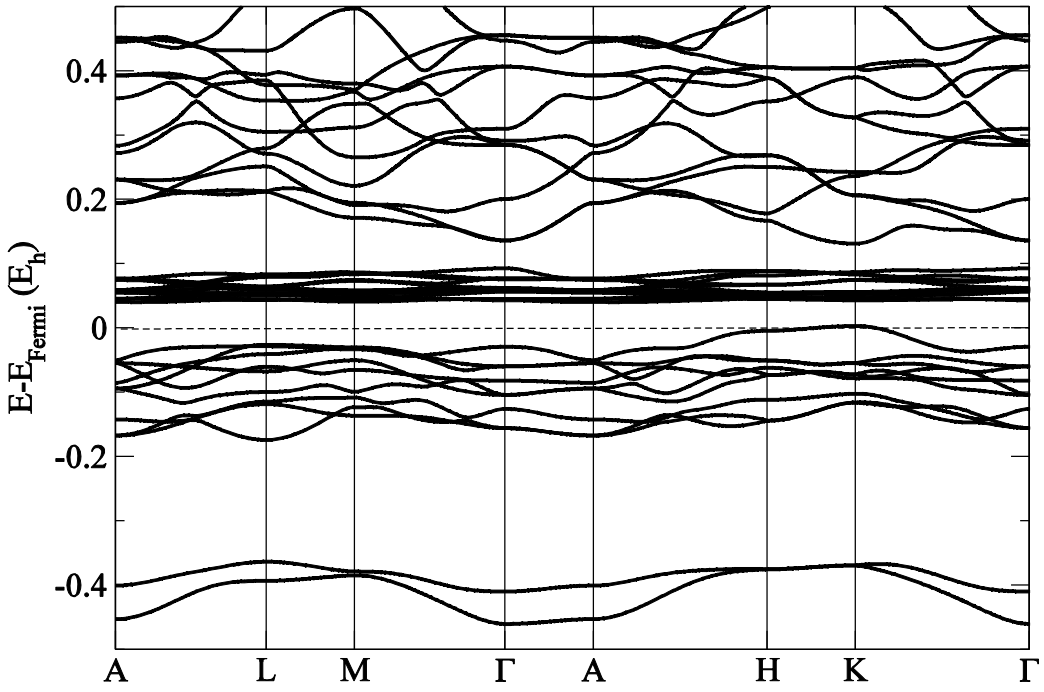


Figure 4. Band structure of the α-Ce_2ON_2 phase. DFT calculations were performed using LDA functional.

4. Conclusion

Detailed investigation of the structure and properties of the α-Ce_2ON_2 have been performed and compared with the related $AlCo_2Pr_2$ phase. Closely related 8-fold coordination of the α-phase has been presented. Mechanical and elastic properties have been calculated at extreme pressures up to 10 GPa. Investigation of mechanical properties of the α-Ce_2ON_2 indicates the ductile character and mechanical stability of this compound. Bulk modulus, shear modulus, and Young's modulus increase more rapidly with the applied pressure, while Poisson's ratio, hardness, and Pugh's criterion increase more gradually with the increase of pressure (0-10 GPa). Electronic properties are characteristic for semiconductor materials with an indirect band gap of ~1.11 eV and studied under high pressures.

Investigated properties are important for future synthesis and possible application of the investigated α-Ce_2ON_2 compound.

Acknowledgments

This research was financially supported by the Ministry of Education, Science, and Technological Development of the Republic of Serbia.

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